

ROOM TEMPERATURE-CURED POLYURETHANE ELASTOMERS

DEPARTMENT OF DEFENSE
PLASTICS TECHNICAL EVALUATION CENTER
PICATINNY ARSENAL, DOVER, N. J.

by: H. R. Bylsma
L. L. Pitchforth, Jr.

presented at: American Chemical Society
Division of Rubber Chemistry
Fall Meeting; October 18, 1962
Paper #25

19960412 143

The Dow Chemical Company
Midland, Michigan

DISTRIBUTION STATEMENT A
Approved for public release;
Distribution Unlimited

DMIC QUALITY INSPECTED 1

PLASTIC 4831

I. BACKGROUND

For almost ten years in the United States, the words "urethane elastomer" have excited new ideas about elastomers which were sought as a panacea to many difficult problems. The majority of research done and papers published have described new materials which were suitable for very abrasive, high tensile strength or high temperature uses. Rubber wheels which were very abrasion resistant, slurry pumps, automotive parts exposed to high temperatures, and top lifts were applications where cost was less important than the actual physical behavior and long life of the formed item.

(27)

Within the last two to three years much more interest has developed in urethane elastomers which are competitive in price and properties with more conventional materials, such as vinyl plastisols, GRS rubber, neoprene, and other more reasonably priced materials. It is this type of research which will be presented here, describing urethane elastomers, which are castable and curable at ambient conditions, to give elastomers having up to 1000 psi tensile strength, 200% to 300% elongation, and less than 1% compression set (Slide 1). These elastomers also incorporate fillers which lower the cost and improve the physical properties.]

II. GENERAL CASTING PROCEDURE

Most elastomer samples made in these studies were centrifugally cast into molds which would then give bubble-free castings. The elastomers were made by mixing polyglycol, filler and isocyanate component; and degassing these materials at room temperature for 10 to 30 minutes. Then up to 1% catalyst was added and stirred in by spatula. The

mixture was cast into the centrifugal mold. The mold was maintained at 55°C. to facilitate the casting of a greater number of specimens in each working day. However, experiments have shown that whether the material was cast at 55°C. or at 25°C., the ultimate physical properties are the same if sufficient time is allotted for them to develop.

Only the ultimate physical properties obtainable will be discussed in this paper, with some of the factors which affect them. Very little time will be spent on discussing exact curing procedures and catalysts. These elastomers have been cured to brick-like solids in less than 2 minutes or formed into slow curing sealant materials by a proper balance of polyglycols and catalyst type and quantity.

III. RAW MATERIALS

The common variety of toluene diisocyanate (Slide 2), a mixture of the 2,4 and 2,6 isomers, was used in these experiments. We limited the type of material to that castable at room temperature. Other materials such as MDI, PAPI, DADI, and other isocyanates were excluded either for reasons of incompatibility in the systems used or because they are solids at room temperature and would require a higher temperature for liquification before casting. Our efforts were aimed strictly at a room temperature castable material which would cure in a short time to give an elastomer being reasonable in price and readily processable.

Polyglycols for these experiments were commercially available polypropylene glycols from The Dow Chemical Company, known under the trademark of "Voranol®" (Slide 3). The "C" indicates in the case of

Voranol CP-260 polyol that the material is a triol and the number following (260) indicates the molecular weight. Materials used were Voranol P-400, Voranol P-1200, Voranol CP-260, and Polyglycol 11-80 RG or combinations of these materials. The two triols are glycerine-based polyglycols.

The catalyst used in these tests was lead naphthenate, a conventional lead drier, available from many sources as 16% or 24% lead concentration. Preliminary tests at Dow have indicated equivalent final elastomer properties using lead naphthenate, lead octoate or dibutyltin dilaurate.

The great multitude of fillers available caused us to arbitrarily limit the number tested to a few that were readily available and do represent a variety of types of materials.

<u>Filler</u>	<u>Trademark</u>	<u>Source</u>
Magnesium Silicate	Talc	Eaton Chemical & Dyestuff
Calcium Carbonate	Duramite	Thompson-Weinmond Company
Calcium Carbonate	Lesamite	Thompson-Weinmond Company
Ground Silica	Sil-Co-Sil # 398	Ottawa Silica Company
Medium Thermal Carbon Black	Sterling MT	Godfrey L. Cabot, Inc.
Medium Thermal Carbon Black	Thermax	Vanderbilt Company, Inc.
Fine Thermal Carbon Black	P-33	Vanderbilt Company, Inc.
Polyvinyl Chloride Dispersion Resin	Norvinyl P2H	Norsk-Hydro, Norway
Polyvinyl Chloride Dispersion Resin	QYNV	Union Carbide, Bakelite Division
Polyvinyl Chloride Dispersion Resin	Vinnol P 100/70	Wacher-Chemie, Germany

IV. COMPONENT VARIABLES (Slide 4)

Two different adducts have been used. One is a triol adduct of Voranol CP-260 prepared by adding the glycol to a 2.5 mole excess of toluene diisocyanate keeping the reaction temperature under 70°C. The other, the diol adduct of Voranol P-400, was formed similarly, using a 1.25 mole excess of toluene diisocyanate.

These urethane elastomers are characterized by containing primary crosslinks from the tri-functional polyols. This crosslinking may be placed on the adduct side, Formulation 1, Slide 4, or on the glycol side, Formulation 2, Slide 4. Some crosslinking is necessary since the polypropylene glycol-based urethanes have lower secondary bond strengths contributed by hydrogen bonding than corresponding polyesters.

The lower viscosity of adducts of Voranol P-400 makes the material easier to handle. A 20% NCO adduct of Voranol P-400 has a viscosity of 2000 cps. or below, while an adduct of Voranol CP-260 with a 27% reactive isocyanate content has a viscosity of 8,000-10,000 cps. The adduct of Voranol P-400 seems to give improved properties over the adduct of Voranol CP-260 for elastomer properties.

POLYGLYCOL ADDUCTS OF TOLUENE DIISOCYANATE

<u>1 Mole</u>	<u>%NCO</u>	<u>TDI/ Glycol Ratio Wgt.</u>	<u>TDI Equiv.</u>	<u>Viscosity, 77° F.</u>
VORANOL CP-260	26.5	3.5	3.5	8,000-10,000 cps.
VORANOL P-400	20.6	1.5	3.45	1,500- 2,000 cps.

V. DISCUSSION

A. Unfilled Systems

These glycol-adduct elastomer combinations have been evaluated both with and without fillers. The unfilled systems are used for general screening because finer distinctions are available between formulations. The first series of curves and data describe unfilled systems and the interplay of factors which relate to their physical properties.

Slide 5 shows the variation of properties by taking a 20% NCO isocyanate adduct of Voranol P-400 and toluene diisocyanate at an NCO/OH ratio of 1.05 with 1% lead naphthenate catalyst and reacting this with Voranol P-1200, including incremental amounts of Voranol CP-260 up to a maximum of 20%. The tensile strength follows a straight line from 150 to 575 psi, from 2 to 20 weight percent of the Voranol CP-260. The tear strength goes through a minimum and then increases to about 40 psi, using a split tear test pulling at 20"/minute.

One of the most interesting factors (Slide 6) concerning this increase in percent of trifunctionality (or weight/branch point) is the curves shown by the Shore A hardness, the percent compression set, the percent compression, and the percent elongation. At about 5 weight percent of Voranol CP-260 or 19 mole percent, an abrupt change in slope takes place in the Shore A hardness curve. We feel that this indicates a change in the packing arrangement of the system. Corresponding with this is the minimum point in the tear strength and an abrupt leveling off in the percent compression set, the percent compression, and the elongation curve.

By following compressive deformation (Slide 7) of the same elastomer at 100 to 500 psi at 22 hours, with a 1/2 hour relaxation (ASTM D-395-55A), it is noticed that the percent compression at this same 5% level also undergoes an abrupt change in slope.

This same comparison also holds for other triols, such as 11-80 RG which is a 700 molecular weight glycerine-based polypropylene oxide addition product. However, here the changes in slope occur at 20 to 30 weight percent of the triol (Slide 8). The circles represent the Voranol CP-260 crosslinked material while the triangles represent the 11-80 RG crosslinked systems.

A comparison of these two systems shows that when plotting the properties as a function of equivalent weight (Slide 9), they are very close to the same general curve; however, there is a limited equivalent weight to which the Polyglycol 11-80 RG system may go.

However, if we plot these same values on a mole percent triol basis (Slide 10), the superiority of Voranol CP-260 becomes apparent over the 11-80 RG when at about 30 mole percent triol, the tear strength increases markedly with additional amounts of the triol, Voranol CP-260, while the Polyglycol 11-80 RG curve is quite flat. A similar effect occurs with tensile strength (Slide 10), but the change of slope is much less dramatic; however, at 50% triol there is a difference of about 100% in their tensile strength, the Polyglycol 11-80 RG giving a tensile strength of 290 psi and the Voranol CP-260 giving a tensile strength of 520 psi.

B. Use of Fillers

When fillers are included, property improvement occurs. The addition of fillers, whether mineral, carbon black, or organic, such as vinyl plastisols, increases the tensile strength, tear strength, and hardness, and decreases the compression under load with little effect on compression set. (Slide 12).

The successive improvement in properties from unfilled, to mineral-filled systems, to carbon black filled systems is demonstrated in Slide 12 with tensile strengths up to 592 psi. This formulation uses a 23.3% NCO toluene diisocyanate adduct of Voranol P-400 with an NCO/OH ratio of 1.10. The filler level is indicated for each formulation. The polyglycol side is a 90/10 mixture of Voranol P-1200 and Voranol CP-260.

The further improvement in properties, principally tensile strength, tear strength and elongation using polyvinylchloride dispersion resins is outlined on Slide 13. The Vinnol P 100/70 resin from Wacher-Chemie gives the best overall properties. The use of these dispersion resins also allows a more imaginative coloration scheme than carbon black.

The raw material cost per pound on a 30% filled basis using the mineral filler as a comparison point is 3% greater using carbon black filler and 19% greater using vinyl dispersion resin filler. Since the mineral filled system has a much higher specific gravity (Slide 14), on a volume basis vinyl dispersion resin use costs 7% more. Carbon black and mineral filler use cost the same.

The improvement in properties by increased crosslinking also is apparent in filled systems. In Slide 15 the use of Sterling MT carbon black filler, with a 1.10 NCO/OH ratio and a 23.3% NCO toluene diisocyanate adduct of Voranol P-400 with a system of Voranol CP-260 and Voranol P-1200 is pictured. The levels of Voranol CP-260 are 5, 10, and 15% of the polyglycol side in both filled and unfilled systems.

Slide 16 gives a comparison of the various tear strengths (ASTM D-624-54 Die A and C with the split tear test, FTMS-601 M4221). Although the absolute value of the split tear test is much lower, in our experience the test is simpler to run, provides excellent correlation and is less dependent upon elongation. It is run at 20 inches/minute in our laboratories.

VI. CONCLUSION

In conclusion, castable, room-temperature cured, polyglycol based, filled urethane elastomers may be formulated to have good tear and compressive strength properties, at adequate elongation and tensile strength levels.

They are suitable in gasketing, encapsulation and structural areas. These urethane elastomers should be evaluated where their room temperature castability is an advantage.

NOTICE

The information in this paper is presented in good faith, but no warranty is given nor is freedom from any patent owned by The Dow Chemical Company or by others to be inferred.

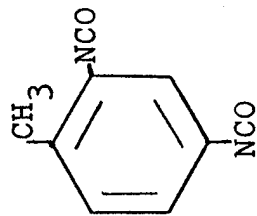
SLIDE 1

Representative Properties

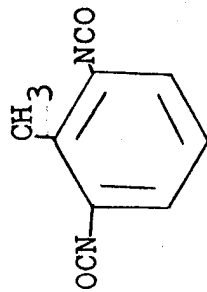
Tensile Strength (ASTM D-530-55T)	20"/minute 1/4" thick dumbbell	< 1000 psi
Elongation (ASTM D-530-55T)		100-350%
Shore A Hardness (ASTM D-676-55T)		45-85
Split Tear (FTMS-601, M-4221)	20"/minute	10-32 pli
Compression Set (ASTM D-395-55A, 400 psi load)		< 1.0%
Filler		Up to 60%
Curing Temperature		< 125°F.
Casting Temperature		Ambient

SLIDE 2

1. Toluene Diisocyanate



2,4 Isomer
80%

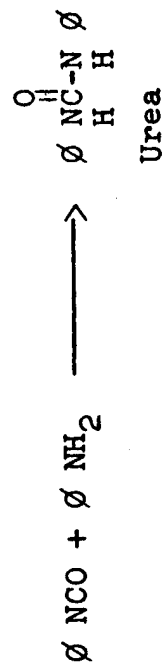


2,6 Isomer
20%

2. Urethane Reactions



Urethane



Urea

SLIDE 3

Dow Polypropylene Glycols

	<u>Functionality</u>	<u>Average Molecular Weight</u>	<u>Average OH No.</u>	<u>Average % OH</u>
VORANOL®P-400	Diol	400	281	8.5
VORANOL P-1200	Diol	1200	93.4	2.83
VORANOL P-2000	Diol	2000	56.1	1.70
VORANOL CP-260	Triol	255	660	20.0
Polyglycol 11-80 RG	Triol	700	241	7.29

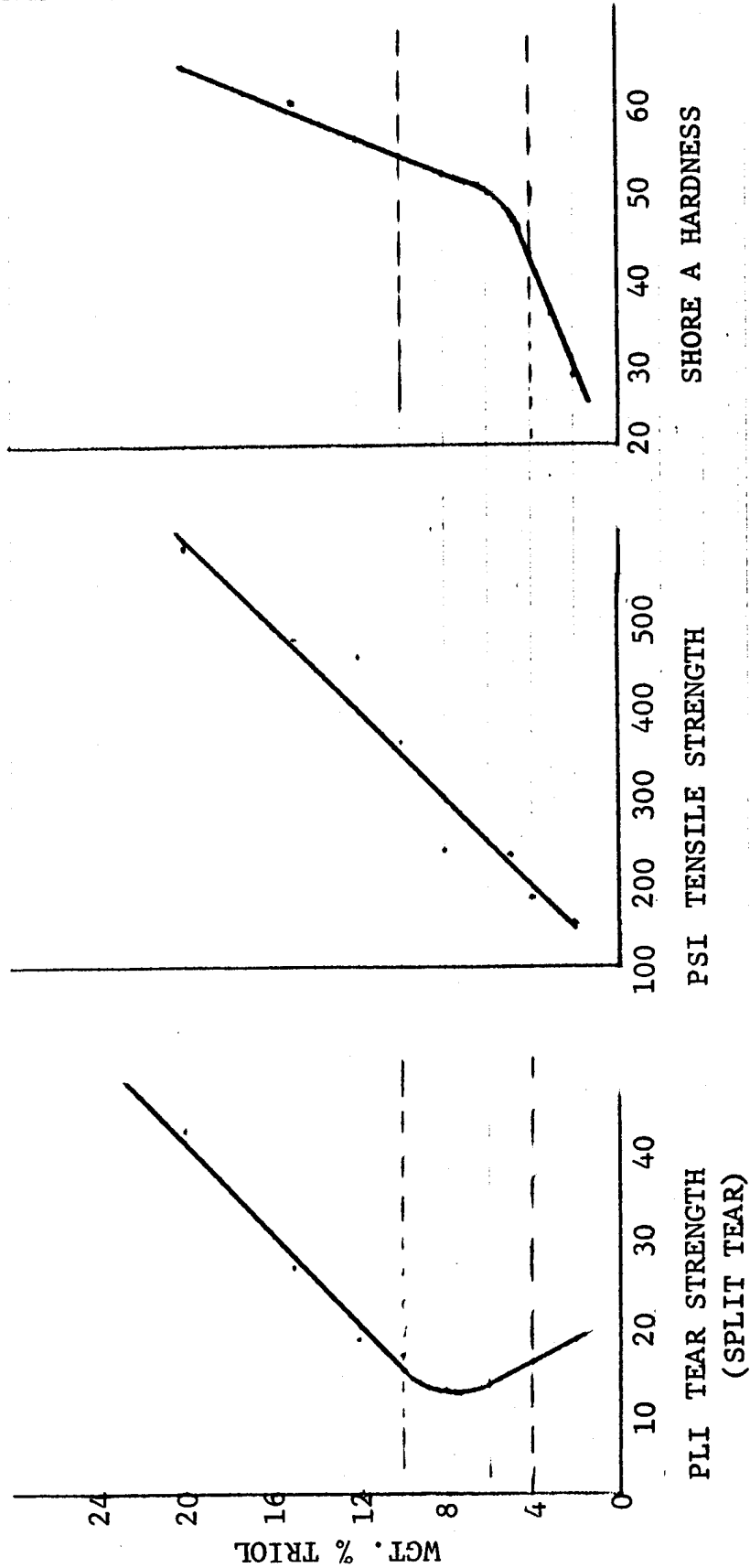
SLIDE 4

Casting System

<u>Isocyanate Component</u>	<u>VORANOL® Polyglycol Component (Includes Filler and Catalyst)</u>
1. VORANOL CP-260 - Adduct of TDI ~27% NCO	P-1200 or P-2000, also CP-260
2. VORANOL P-400 - Adduct of TDI ~18-21% NCO	CP-260 with P-1200 or P-2000

SLIDE 5

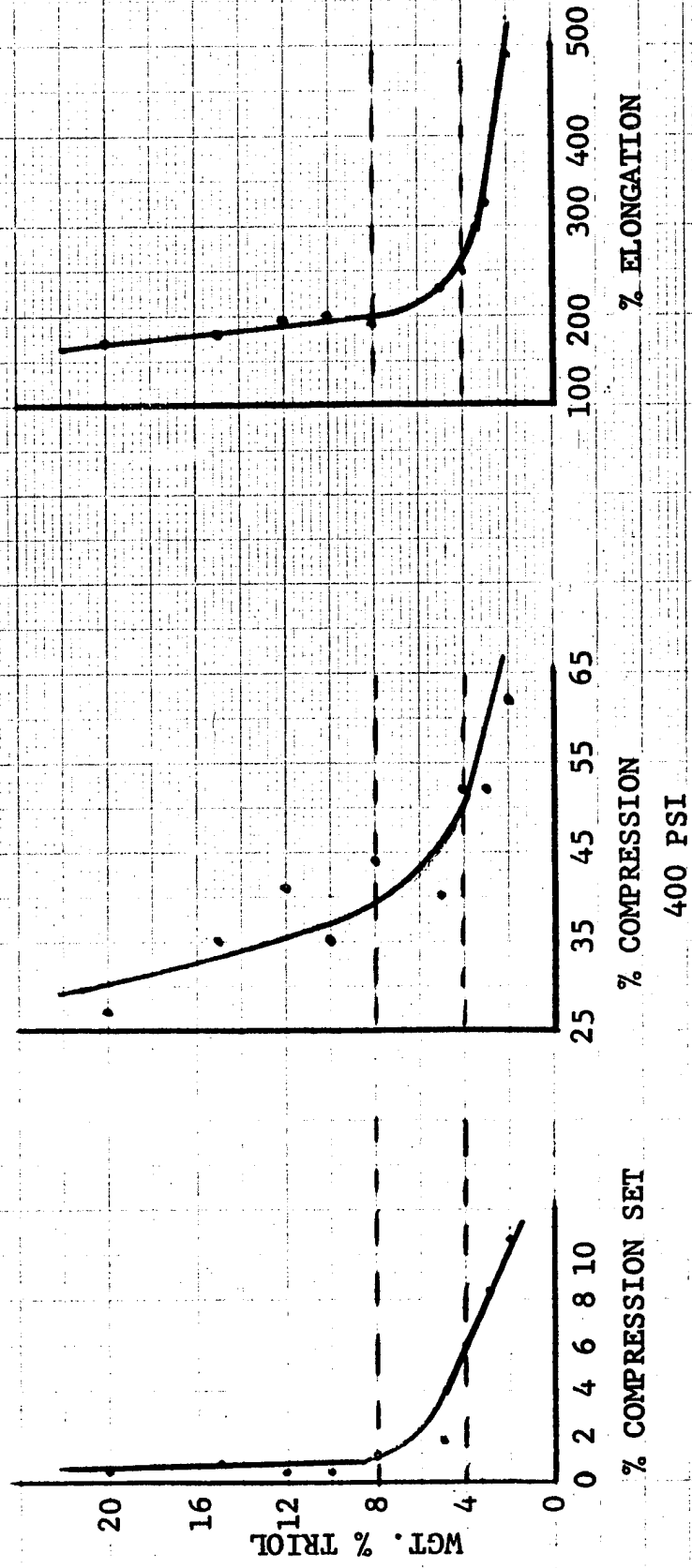
CROSSLINKING VS. PHYSICAL PROPERTIES



VORANOL®CP-260 IS THE TRIOL

SLIDE 6

CROSSLINKING VS. PHYSICAL PROPERTIES

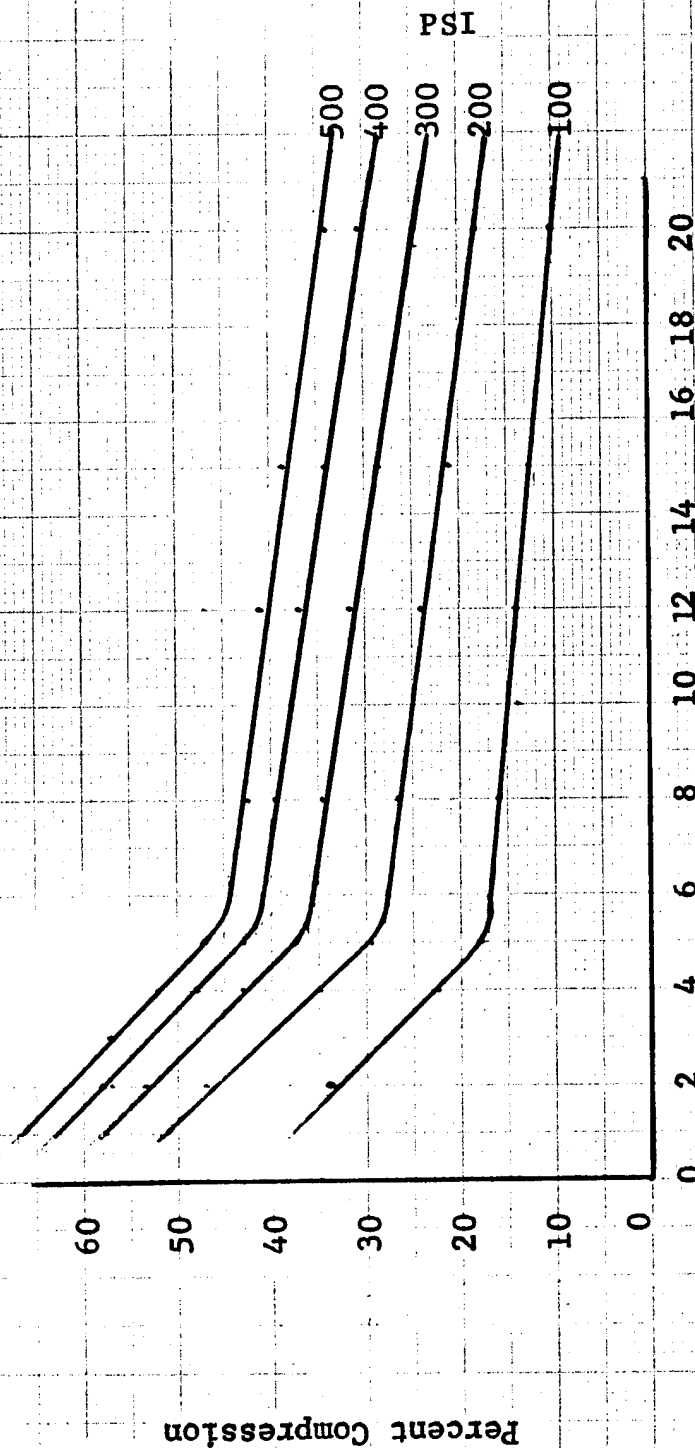


VORANOL®CP-260 IS THE TRIOL

SLIDE 7

COMPRESSIVE DEFORMATION

NCO/OH Ratio 1.05
Adduct 20% NCO, TDI with VORANOL® P-400
Polyglycols
VORANOL P-1200
VORANOL CP-260



Weight Percent VORANOL CP-260

SLIDE 8

COMPARISON OF TRIOLS IN VORANOL® P-1200

- VORANOL CP-260 (260 mol. wgt.)
- ▲ Polyglycol 11-80 RG (700 mol. wgt.)

NCO/OH Ratio

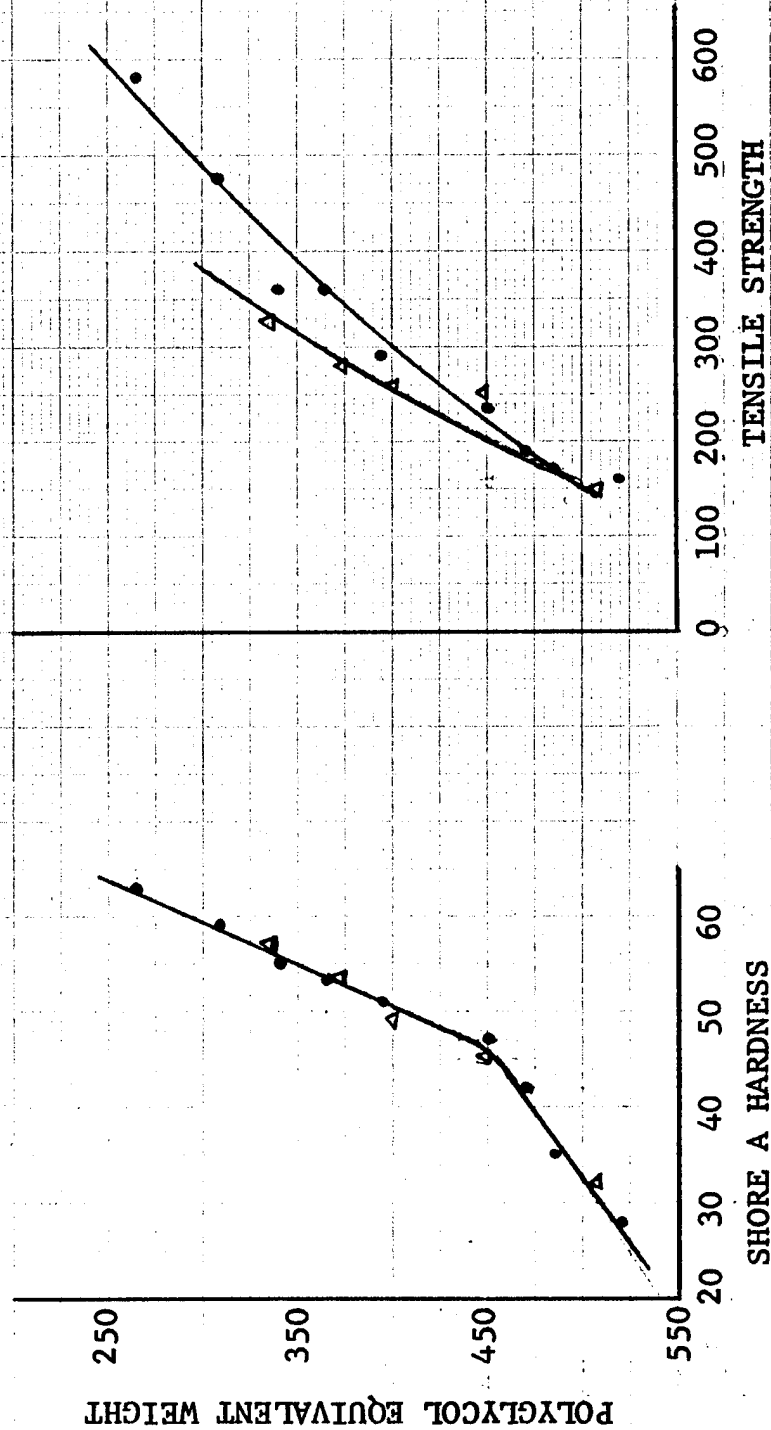
1.05

Adduct

20% NCO

TDI with

VORANOL P-400



SLIDE 9

COMPARISON OF TRIOLS IN VORANOL® P-1200

◦ VORANOL CP-260 (260 mol. wgt.)

Δ Polyglycol 11-80 RG (700 mol. wgt.)

NCO/OH Ratio

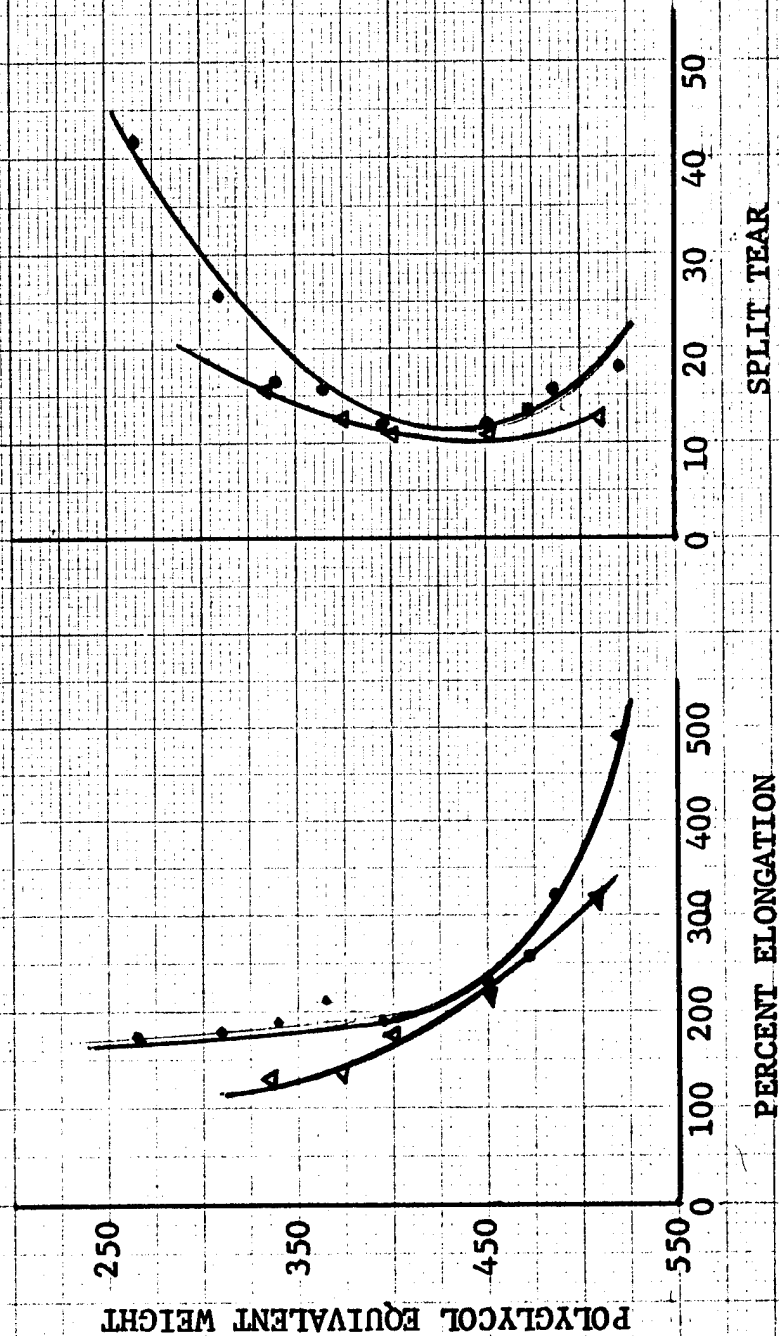
1.05

Adduct

20% NCO

TDI with

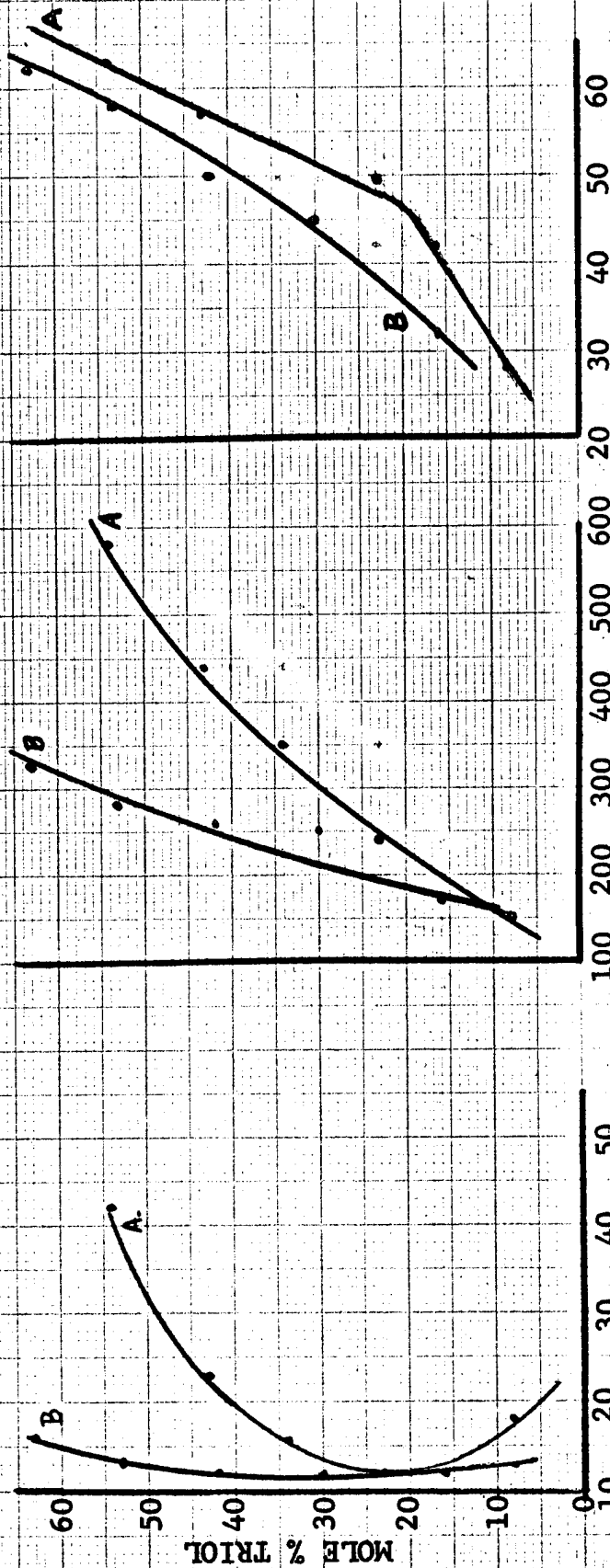
VORANOL P-400



SLIDE 10

PROPERTY COMPARISON

- A. VORANOL® P-1200 - VORANOL CP-260
- B. VORANOL P-1200 - Polyglycol 11-80 RG

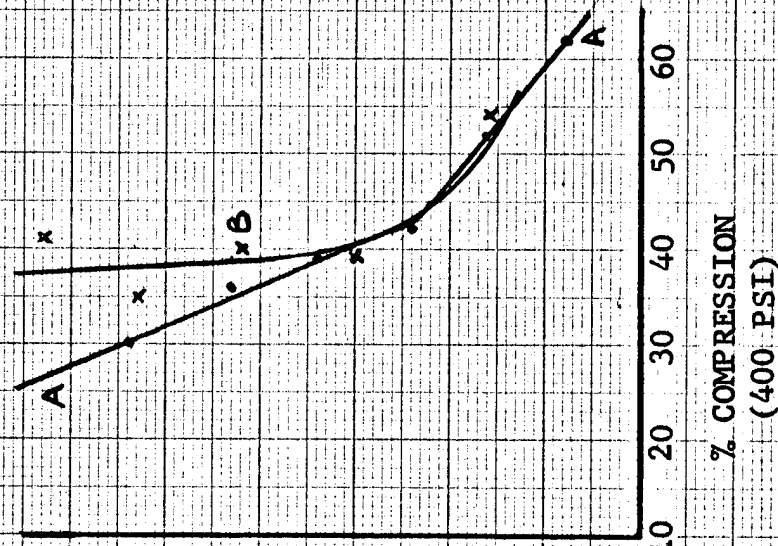
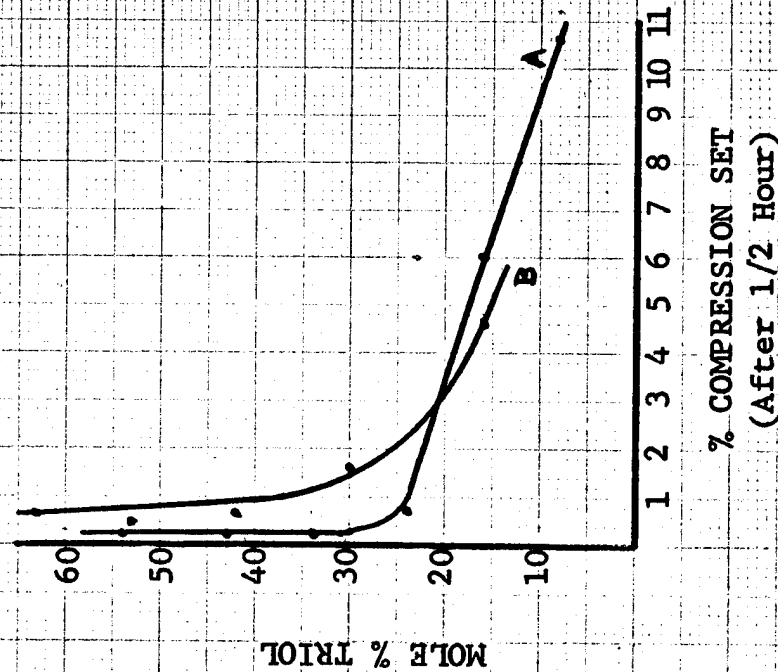


SLIDE 11

PROPERTY COMPARISONS

A. VORANOL®P-1200 - VORANOL CP-260

B. VORANOL P-1200 - Polyglycol 11-80 RG



SLIDE 12

Physical Properties

Filler	Specific Gravity	Shore A Hardness	Tear pli	Tensile psi	Elongation %	Compression	
						Underload	% Set
None	1.10	57	13.9	238	185	40	0.4
10% Sterling MT*	1.15	62	18.2	448	203	30	0.8
18.2% Sterling MT*	1.18	64	21.1	438	210	30	1.0
18.2% P-33*	1.18	65	21.0	562	200	30	1.2
30% Thermax*	1.24	72	23.0	571	145	30	1.2
30% Sterling MT*	1.25	73	24.6	592	160	24	1.6

23.3% NCO TDI adduct of VORANOL®P-400

90/10 VORANOL P-1200 and VORANOL CP-260

1.05 NCO/OH Ratio

*Carbon black

SLIDE 13

Physical Properties (Cont.)

<u>Filler</u>	<u>Specific Gravity</u>	<u>Shore A Hardness</u>	<u>Tear pli</u>	<u>Tensile psi</u>	<u>Elongation %</u>	<u>Compression</u>	
						<u>Underload</u>	<u>% Set</u>
30% Sterling MT*	1.25	73	24.6	592	160	24	1.6
30% Norvinyl P2H**	1.17	66	31.3	485	243	28	1.8
30% QYNV**	1.17	73	27.2	599	178	30	1.2
30% Vinnol P 100/70**	1.17	75	26.6	843	190	24	0.8

23.3% NCO TDI adduct of VORANOL®P-400

90/10 VORANOL P-1200 and VORANOL CP-260

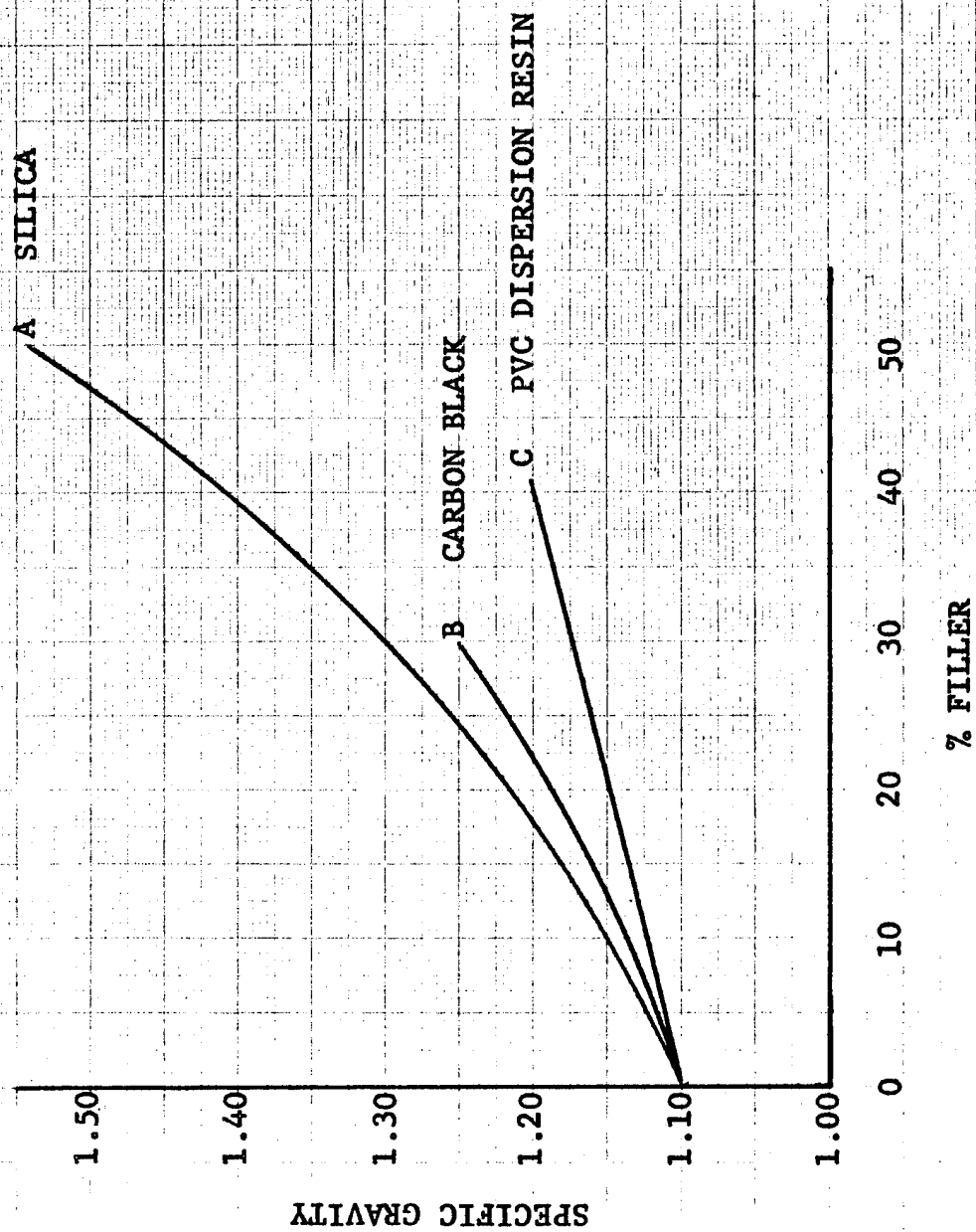
1.05 NCO/OH Ratio

*Carbon black

**Polyvinyl chloride dispersion resins

SLIDE 14

SPECIFIC GRAVITY VS. % FILLER



SLIDE 15

Crosslinking and Physical Properties

<u>Ratio Triol/Diol</u>	<u>Filler</u>	<u>Shore A Hardness</u>	<u>Tear pli</u>	<u>Tensile psi</u>	<u>Elongation %</u>	<u>Compression</u>	
						<u>Underload</u>	<u>% Set</u>
5/95	30%	67	21.5	542	222	34	1.0
10/90	30%	73	24.6	592	160	24	1.6
15/85	30%	79	32.6	627	98	17	1.0
5/95	---	47	12.2	233	230	40	1.8
10/90	---	53	15.5	356	203	35	0.4
15/85	---	59	25.5	478	182	35	0.8

Filler - Sterling MT Carbon Black

NCO/OH Ratio - 1.10

Adduct - 23.3% NCO TDI with VORANOL®P-400

VORANOL P-1200 Diol

VORANOL CP-260 Triol

SLIDE 16

Comparison of Tear Strength Methods

<u>Filler</u>	<u>Shore A Hardness</u>	<u>Tear Strength</u>		
		<u>Split¹ Tear</u>	<u>Die A²</u>	<u>Die C²</u>
Unfilled	46	10.0	-	-
33% Duramite	57	12.8	53	86
33% Sil-Co-Sil No. 398	58	14.0	55	67
33% Talc	66	16.9	60	80
33% Sterling MT	64	20.1	74	136

¹FTMS-601 M 4221

²ASTM D-624-54

1.10 NCO/OH ratio

23.3% NCO toluene diisocyanate adduct of VORANOL® P-400

80/20 VORANOL P-1200 and Polyglycol 11-80 RG

SLIDE 17

SUMMARY

1. An inexpensive castable urethane elastomer.
2. Ambient temperature casting and curing.
3. Wide property spectrum by simple changes in the triol content.
4. Upgrading of properties and cost reduction by filler addition.